ACTIVATION OF SEPIOLITE BY VARIOUS ACID TREATMENTS

C.Kalaiselvi[1], M.Sivakumar[2], R.Subadevi[3]

[1,2,3] #120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi- 630003. Tamil Nadu, India.
(Corresponding Author(s): susimsk@yahoo.co.in (R.Subadevi) ; susiva73@yahoo.co.in (M.Sivakumar))*

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Abstract - *The rechargeable Li-S battery is an attractive candidate for the next generation of energy storage device. Li-S battery based on redox coupling has high theoretical specific capacity and energy density. Large volumetric expansion of sulfur coupled with polysulphide dissolution during lithiation process is one among the problems faced by Li-S battery. To come across this issue, conducting additive materials are used as a positive electrode with sulfur. In this work, sieved sepiolite has been selected for sulfur based composite material to face the above provocation. Sepiolite is a hydrated magnesium silicate clay mineral with layered chain structure and fibrous morphology. It could be an absorbing material for lithium – sulfur batteries due to its ion transmission channel and large pore volume. Sepiolite was activated with different acid treatment (HCl, H_2SO_4, and HNO_3) to employ as cathode materials, in order to improve cyclability of Li-S batteries. The obtained composites are characterized by using XRD, FT-IR and SEM analyses. In XRD pattern, acid treatment increases the surface area, because it virtually destroys the minerals and produces amorphous silica. The functional vibrations of the prepared composites are analyzed by FT-IR spectra. The fibrous morphology of the particles was observed by SEM images.*

***Key Words*: Lithium sulfur battery, energy density, polysulphide, sepiolite, acid treatment**,

1. INTRODUCTION

Li-S battery is an electrochemical storage device through electrical energy can be stored in sulfur electrode [1]. These batteries have gained intense attention, because they have a high theoretical energy than that of current Li-ion cells. This is due to the very high specific capacity 1675mAh/g based on two electron reaction [2]. In addition, sulfur is low cost, plenteous, safety and environmental compatibility are some of the most important parameters [3].However, Li-S batteries also bear from numerous tribulations. One among this crisis was high solubility of the intermediate products of lithium polysulfides in the organic electrolyte lowers the consumption of sulfur and hence results in poor cycle performance of the batteries [4]. Sulfur and lithium sulfide are both insulators, which necessitates the incorporation of conductive additives into the electrodes [5]. To overcome the insulation of sulfur hub on introducing electrical conductive additives are used. Micropores act as the host of the impregnated sulfur and prevent the dissolution of polysulfides. In the present study, sieved sepiolite was used as an additive material to develop the above inherent troubles.

Sepiolite (Sep) is a hydrated magnesium silicate having the half-unit cell chemical formula of $Mg_4Si_{12}O_{30}(OH)_4.12H_2O$[7-9].Sep is categorized in natural clay minerals with the needle-like or fiber-like morphology consisting of several blocks and tunnels which are oriented toward the fiber axis. This has been commonly used in several technological and industrial applications. The surface of sepiolite has a great ability for grafting reactions with organosilanes due to its high content of silanol groups that are very susceptible to the reactions [10]. Many of these applications are based on the good adsorptive, rheological and catalytic properties [11,12]. The development of the porosity and of the number of acid centres and the size of the silica fibres in the solids are characterized as a function of the acid activation. The Lithium-sulfur battery is a liquid electrochemical system, in which the dissolution of lithium polysulfide plays an essential role in the battery performance [6].

2. EXPERIMENTAL WORK

2.1. Material preparation:

Sepiolite powder was purchased from Sigma-Aldrich, different acids (HCl, H_2SO_4 and HNO_3) from Nice Company, Sulfur Alfa-Aaser.

Acid treatment

Conc. Hydrochloric acid (5ml) and 10ml of deionised water were mixed vigorously and then getting dilutes hydrochloric acid. The 10ml of dilute HCl were added to the 1 gram of sieved sepiolite material. After that, without disturbing the mixing material for a particular time at room temperature and then centrifugation process for filtering and washed with deionised water. Finally, we get the particles and then dried at 40°C for 5 h in vacuum oven.

Thermal treatment:

Pre-activated sieved sepiolite/Sulfur were uniformly mixed and placed in a ceramic boat and then heated to 155° C in the Ar gas introduced into the tubular furnace for 12 hrs and 320° C for 6 hrs. The sample is heat treated by two step process.

2.2 Characterization:

The structure and composition of the pre-treated sieved sepiolite/sulfur was synthesized by using X-ray Diffractometer (PAN Analytical XPERT-PRO with Cu Kα radiation). The spectra range between 4000-400 cm^{-1} was examined by FT-IR Spectrophotometer (Thermo Nicolet 380). The structural morphology was characterized by Scanning electron microscope (Quanta FEG 250).

3. RESULT AND DISCUSSION:

XRD:

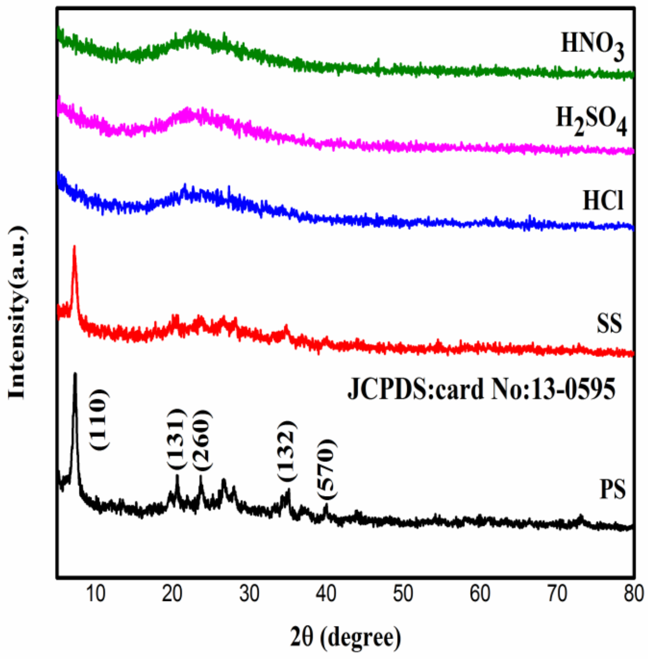

Fig -1: shows the XRD patterns of pure, sieved and different acid treatment

Figure1. shows the XRD patterns of pure, sieved and different acid treatments were analysed. In the XRD pattern of the pre-treated sieved sep/sulfur, we could clearly observed that the diffraction peaks were disappeared. The intensity of peak has no obvious chances when the temperature is above 400°C [13,14]. Acid treatment has been widely used to modify sepiolite for the purpose to disaggregate the clay particles, eliminate mineral impurities, and remove metal-exchange cations, exchange proton, and enhance the surface area of clay minerals. In order to examine the acid activation, the effect of acid treatment on strength was investigated[5]. The elimination of sepiolite structure and formation of silica occurs during acid treatment.

FT-IR:

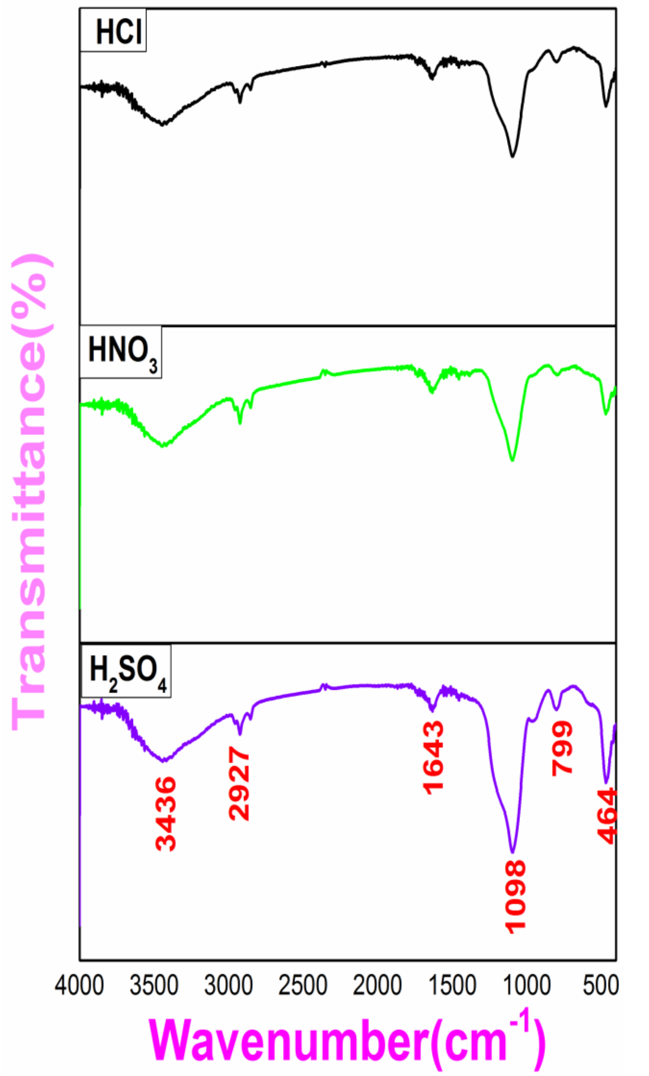

Fig -2: FT-IR spectra of different acid treatment

FT-IR spectra of pretreated sepiolite of different acid treatments are illustrated in the figure.2.The bands 3436 cm^{-1} are attributed to the presence of different types of water molecules in the structure of the mineral (adsorbed and zeolitic water) octahedral coordinated OH to Mg and edge Mg-OH[16,17]. Absorption bands at2927 cm^{-1} are due to C-H stretching vibrations. The band at 1663 cm^{-1} due to the bending vibration mode of zeolitic water underwent similar simplification process. These were clearly weakened by increasing the thermal treatment and almost disappeared at the temperature above 500°C. The absorption peak around 1098 cm^{-1} gradually disappeared which implies that the tetrahedral skeleton was destroyed. Besides, the appearance of absorbance bands at 799 cm^{-1} indicated the presence of quartz in sepiolite[18]. The bands at 1098 cm^{-1} and 464 cm^{-1} represent the stretching vibrations of Si-O-Si groups of the tetrahedral sheet.

SEM:

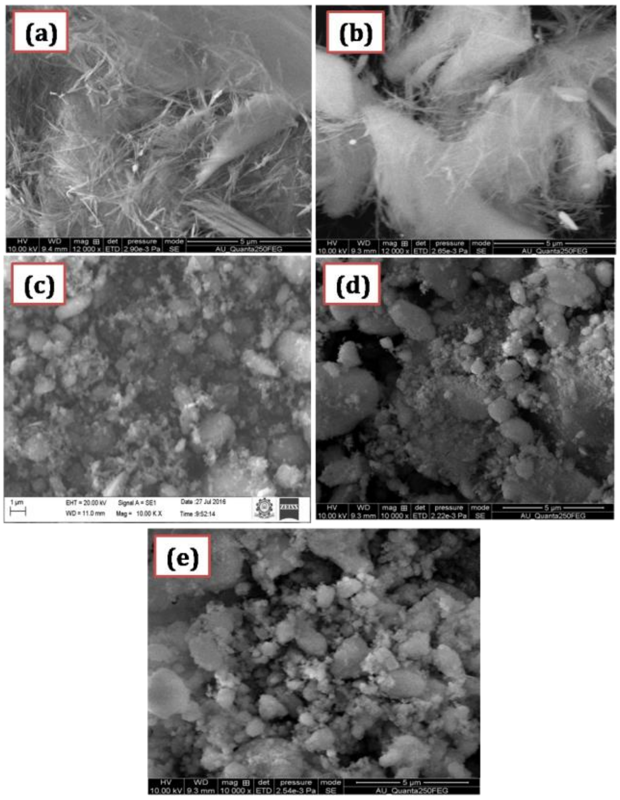

Fig-3: SEM images of (a) pure sepiolite (b) sieved sepiolite (c) pre-treated HCl/sep/S (d) pre-treated H_2SO_4/sep/S (e) pre-treated HNO_3/Sep/S

Figure.3. shows the morphology of after sulfur injection by different acid treatments. The needle–like fibrous clusters are observed in the pure and sieved sepiolite materials. We can see that the sepiolite powders are composed of short micro fibrous bundles and also small spherical tiny particles are presented in the SEM analyses [19]. After moderate thermal activation the fibrous morphology is still retained, but the dispersion degree of fibrous crystal was improved. However, with the increase of thermal treatment temperature, the fibers become shorter and the aggregation degree also increased. Therefore, the appropriate thermal treatment temperature is significant to improve the pore structure and surface properties of sepiolite [20].

4. CONCLUSION:

The pre-treated sieved sepiolite /sulfur material was prepared by Acid and thermal heat treatment method. These samples were characterized by XRD, FT-IR, and SEM. In the XRD pattern we observed that, sulfur peaks were completely disappeared in the pattern due to the restraint in the mesoporous sepiolite. Various acid and thermal treatments reveals the formation of amorphous silica. The functional vibrations of the prepared materials were analysed by FT-IR spectra. It conforms, water molecules are released and structural deformation was occurred. The fibrous morphology of the particles was observed through SEM images. It shows, pre-treated sepiolite/sulfur is composed of short and small spherical particles. From these it concludes, pre-acid treated sepiolite and sulfur mixed cathode to be a good candidate for the Lithium Sulfur Battery.

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